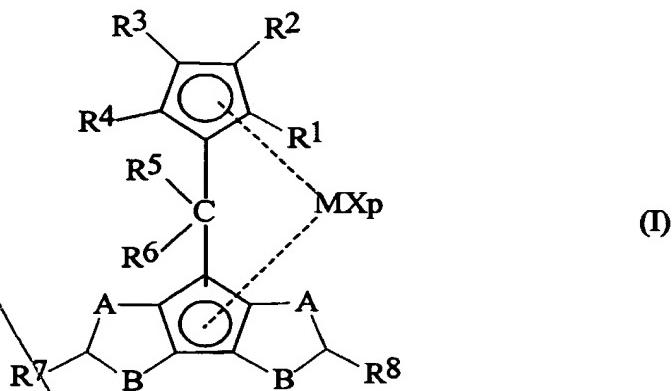


CLAIMS

Scribble

- a process for the preparation of polymers of ethylene comprising the polymerization reaction of ethylene and optionally one or more olefins in the presence of a catalyst comprising the product obtainable by contacting:

(A) metallocene compound of formula (I):



wherein

the rings containing A and B have a double bond in the allowed position having an aromatic character;

A and B are selected from sulfur (S), oxygen (O) and CR⁹, R⁹ being selected from hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is CR⁵ or if B is S or O, A is CR⁵;

R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ which may be the same as or different from each other, are selected from hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, and two adjacent R¹ and R² and/or R³ and R⁴ and/or R⁵ and R⁶ can form a ring comprising 4 to 8 atoms, which can bear substituents;

M is an atom of a transition metal selected from those belonging to group 3, 4, 5, 6 or to the lanthanide or actinide groups in the Periodic Table of the Elements (new IUPAC version),

X, which may be the same as or different from each other, is hydrogen, halogen atom, a R¹⁰, OR¹⁰, OSO₂CF₃, OCOR¹⁰, SR¹⁰, NR¹⁰₂ or PR¹⁰₂ group, wherein the substituents R¹⁰

Sub A(17)
cont.

are selected from hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

p is an integer of from 1 to 3, being equal to the oxidation state of the metal M minus 2; isopropylidene(cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride being excluded;

and

(B) an alumoxane and/or a compound capable of forming an alkyl metallocene cation.

2. The process according to claim 1, wherein in the metallocene compound of formula (I) the transition metal M is selected from titanium, zirconium and hafnium.

3. The process according to any of claims 1 to 2, wherein in the metallocene compound of formula (I) the X substituents are chlorine atoms or methyl groups.

4. The process according to any of claims 1 to 3, wherein in the metallocene compound of formula (I) A and B are selected from sulfur and a CH group, either A or B being different from CH, R⁵ and R⁶ are C₁-C₂₀-alkyl groups, and R⁷ is equal to R⁸.

The process according to claim 4, wherein R¹, R³ and R⁴ are hydrogen, R⁵ and R⁶ are methyl, R² is C₁-C₂₀-alkyl groups and R⁷ and R⁸ are hydrogen or methyl groups.

The process according to any of claims 1 to 5, wherein said alumoxane is obtained by contacting water with an organo-aluminium compound of formula H_jAlR¹²_{3-j} or H_jAl₂R¹²_{6-j}, where R¹² substituents, same or different, are hydrogen atoms, C₁-C₂₀-alkyl, C₃-C₂₀-cyclalkyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl, optionally containing silicon or germanium atoms with the proviso that at least one R¹² is different from halogen, and j ranges from 0 to 1, being also a non-integer number.

7. methylalumoxane (MAO), tetra-(isobutyl)alumoxane (TIBAO), tetra-(2,4,4-trimethylpentyl)alumoxane (TIOAO), tetra-(2,3-dimethylbutyl)alumoxane (TDMBAO) and tetra-(2,3,3-trimethylbutyl)alumoxane (TTMBAO).

8. The process according to any of claims 1 to 5, wherein the compound capable of forming a metallocene alkyl cation is a compound of formula D⁺E⁻, wherein D⁺ is a Brønsted acid, able to give a proton and to react irreversibly with a substituent X of the metallocene of formula (I) and E⁻ is a compatible anion, which is able to stabilize the active catalytic species originating from the reaction of the two compounds, and which is

*Sub A18
cont.*

sufficiently labile to be able to be removed by an olefinic monomer.

*Sub A19
cont'd*

The process according to claim 8, wherein the anion Z^- comprises one or more boron atoms.

Sub A19

10. The process according to any of claims 1 to 9, wherein the process is carried out in the presence of an alpha-olefin selected from propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene and 1-dodecene.

*Sub D2
cont'd*

11. The process according to claim 10, wherein said alpha-olefin is 1-hexene or propylene.

12. The process according to claim 10, wherein the molar content of alpha-olefin derived units is between 0% and 60%.

*Sub A20
cont'd*

13. The process according to any of claims 1 to 9, wherein the process is carried out in the presence of a cyclic comonomer.

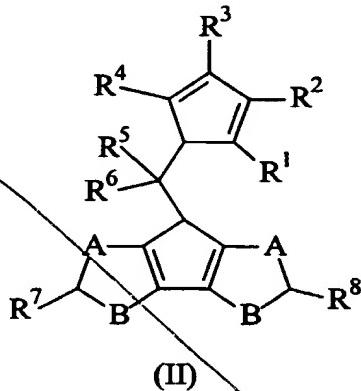
*Sub D2
cont'd*

14. The process according to claim 13, wherein the cyclic comonomer is 5-ethyliden-2-norbornene.

*Sub A21
cont'd*

15. The process according to claims 13 or 14, wherein the molar content of the cyclic comonomer is between 0mol% and 30mol%.

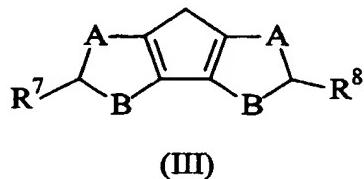
16. A process for the preparation of a ligand of formula (II):



and/or its double bond isomers,

wherein A, B, R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and R⁸ are defined as in claims 1-5, comprising the following steps:

- i) treating the compound of formula (III) with at least one equivalent of a base;

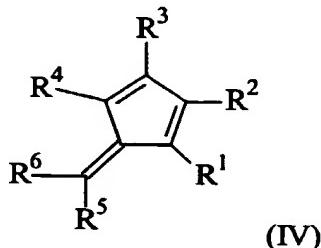


wherein the rings containing A and B have a double bond in the allowed position

ii)

*Sub A21
cont.*

having an aromatic character; A, B, , R⁷ and R⁸ are defined as in claims 1-5;
 contacting the thus obtained corresponding anionic compound of formula (III)
 with a compound of formula (IV):

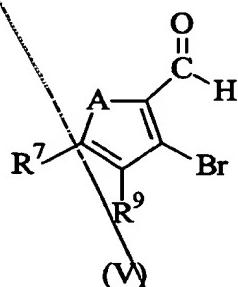


wherein R¹, R², R³, R⁴, R⁵ and R⁶ are defined as in claims 1-5, and

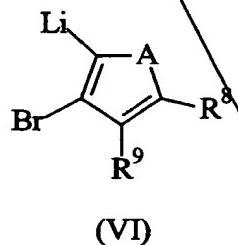
iii) treating the thus obtained product with a protonating agent.

17. The process for the preparation of a ligand of formula (II) according to claim 16 wherein
 The base used in step i) is selected from hydroxides and hydrides of alkali- and earth-alkali metals, metallic sodium and potassium and organometallic lithium salts and the
 protonating agent used in the above process is a quaternary ammonium salt.
18. A process for preparing the compound of formula (III) as defined in claim 16 wherein B
 is a CR⁹ group comprising the following steps:

i) treating a compound of formula (V):



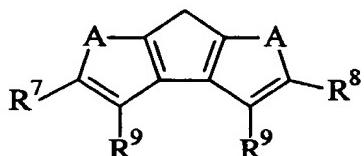
wherein A is sulfur or oxygen, with a compound of formula (VI):



wherein A is sulfur or oxygen,

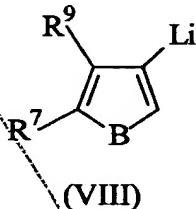
ii) contacting the thus obtained product with a reducing agent in a molar ratio

- Sub A1
cont.*
- iii) between said reducing agent and the product obtained under I) of at least 1;
 - iv) contacting the product obtained under ii) with a compound selected from an organolithium compound, sodium and potassium in a molar ratio between said compound and the product obtained in step ii) of equal to or greater than 2;
 - treating the thus obtained product with an agent selected from the group consisting of copper chloride, iodine and Mg/Pd., in order to obtain a compound of general formula (VII):



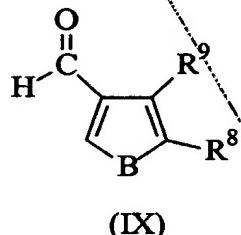
(VII)

19. A process for preparing the compound of formula (III) as defined in claim 16 wherein B is sulfur or oxygen and A is a CR⁹ group comprising the following steps:
- v) contacting a compound of formula (VIII):



(VIII)

wherein B is sulfur or oxygen,
with a compound of formula (IX):

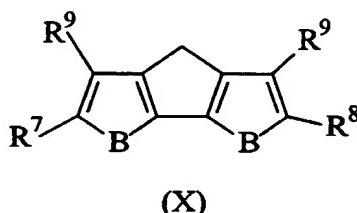


(IX)

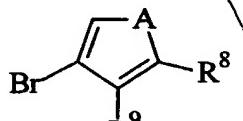
wherein B is sulfur or oxygen,
and subsequently treating with a neutralization agent;

- vi) treating the thus obtained product with a reducing agent in a molar ratio between said reducing agent and the compound obtained under i) of at least 1;
- vii) contacting the thus obtained product with a mixture of an organolithium compound and tetramethylethylenediamine (TMEDA) in a molar ratio between

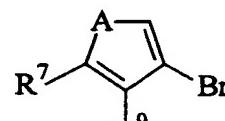
- Sub A1 part 1*
- viii) said mixture and the product obtained under ii) of at least 2, contacting the thus obtained product with an agent selected from the group consisting of copper chloride, iodine and Mg/Pd., in order to obtain a compound of formula (X):



- 20 A process for preparing the compound of formula (III) as defined in claim 16 wherein A is sulfur or oxygen and B is a CR⁹ group comprising the following steps:
- i) contacting an equimolar mixture of compounds of formulae (XI) and (XII):



and



XII

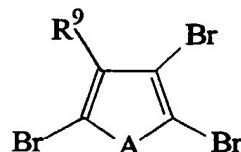
wherein A are sulfur or oxygen,
with a Lewis acid or a mixture of a Lewis acid and a protonic acid;

- ii) treating the thus obtained product with CH₂O in a molar ratio between said mixture and CH₂O of a range between 10:1 and 1:10;
- iii) contacting the thus obtained product with a compound selected from an organolithium compound, sodium and potassium;
- iv) contacting the thus obtained product with an agent selected from the group consisting of copper chloride, iodine and Mg/Pd., in order to obtain a compound of general formula (VII)
21. The process according to claim 20, wherein the Lewis acid is selected from zinc dichloride, cadmium dichloride, mercury dichloride, tin tetrachloride, trifluoroborane, zirconium tetrachloride, titanium tetrachloride.
22. A process for the preparation of a metallocene compound of the formula (I): comprising the following steps:

- Sub A1
cont.*
- a) contacting a compound of formula (II) as defined in claim 16 with a base, wherein the molar ratio between said base and the compound of formula (II) is at least 2;
 - b) contacting with a compound of formula MX_{p+2} , M and X being defined as in claim 1 and p is an integer being equal to the oxidation state of the metal M minus 2.

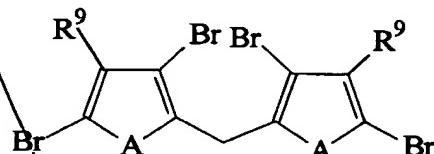
23 A process for preparing the compound of formula (III) as defined in claim 16 wherein A is sulfur or oxygen and B is a CR^9 group comprising the following steps:

- i) contacting a compound of formula (XIII):



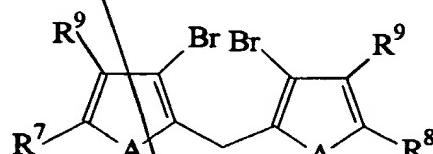
(XIII)

with a base selected from an organolithium compound, sodium or potassium; treating with a formic ester, wherein the molar ratio between said ester and the compound of formula (XIII) is at least 1:2, and subsequently treating the obtained product with a reducing agent in order to obtain a compound of formula (XIV):



(XIV)

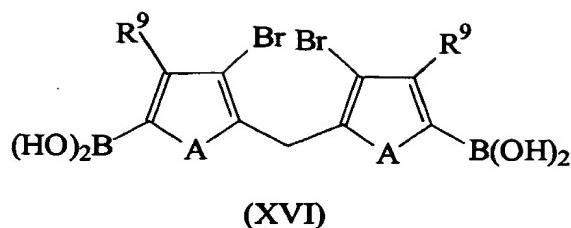
- iii) contacting the compound of formula (XIV) with a base selected from an organolithium compound, sodium or potassium and subsequently treating the dimetallated compound with an alkylating agent to obtain the compound of formula (XV);



(XV)

or alternatively treating the dimetallated compound with an ester of boric acid and a protonating agent in order to obtain the compound of formula (XVI):

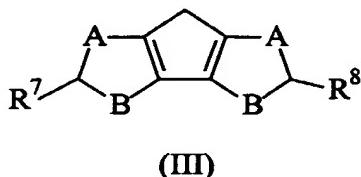
*Sub A1
cont.*



and subsequently contacting with a mixture of an alkylating agent in the presence of an transition metal complex compound for obtaining the compound of formula (XV);

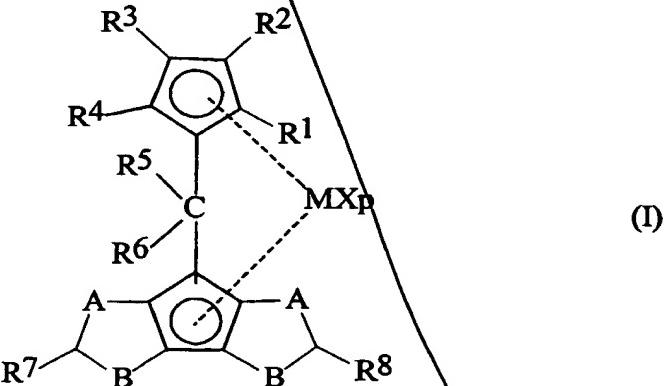
- iii) contacting the alkylated compound obtained by step b) with a coupling agent; agent selected from the group consisting of copper chloride, iodine and Mg/Pd in order to obtain the compound of formula (VII).

24. A compound of formula (III)



wherein the rings containing A and B have a double bond in the allowed position having an aromatic character; A and B are described in claims 1-5 and R⁷, and R⁸ which may be the same as or different from each other, are selected from a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements.

25 A metallocene compound of formula (I):

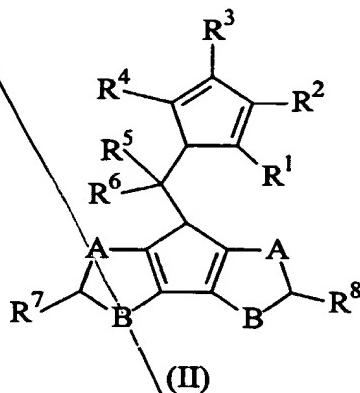


wherein A, B, M, X, p, R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, and R⁹ have the meaning as in claims 1-5; isopropylidene(cyclopentadienyl)-7-(cyclopentadithiophene)zirconium

Sub A1 cont.

dichloride,
 isopropylidene(3-methyl-cyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride;
 isopropylidene(3-ethyl-cyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride;
 isopropylidene(3-t-butyl-cyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride;
 isopropylidene(3-n-butyl-cyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride;
 isopropylidene(3-trimethylsilyl-cyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride and
 isopropylidene (3-i-propylcyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride being excluded.

26 a ligand of formula (II):



and/or its double bond isomers,

wherein the rings containing A and B have double bonds in any of the allowed position, having an aromatic character and A, B, R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and R⁸ have the meaning as in claims 1-5; isopropylidene(cyclopentadiene)-7-(cyclopentadithiophene), isopropylidene(3-methyl-cyclopentadiene)-7-(cyclopentadithiophene); isopropylidene(3-ethyl-cyclopentadiene)-7-(cyclopentadithiophene); isopropylidene(3-t-butyl-cyclopentadiene)-7-(cyclopentadithiophene); isopropylidene(3-n-butyl-cyclopentadiene)-7-(cyclopentadithiophene); isopropylidene(3-trimethylsilyl-cyclopentadiene)-7-(cyclopentadithiophene) and isopropylidene (3-i-propylcyclopentadienyl)-7-(cyclopentadithiophene) being excluded.